Van der Waals Model of a Fluctuation Gas Close to the Critical Point

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According to the fluctuation theory of phase transitions [1] a substance close to the critical point is a gas of the fluctuation clusters. The energy of the fluctuation clusters has the form of ideal gas law $F_f = Nk_{BT} = C_0 R_c^{-3}$. It is on the basis of this equation that the symmetrical scaling equation of state of substance $\Delta\rho_0 (t, \Delta\mu) = dF_f / d\mu$ was obtained. Van der Waals ideas [2] concerning the proper volume of the fluctuation clusters and interacting forces between them at distances $r > R_c$ have been used for the first time in the work [3] for extending the range of application the symmetrical scaling equation of state. Due to this in the work [3] the following expression for fluctuation part of thermodynamic potential was obtained:

$$F_1 = C_0 R_c^{-3} [1 \quad | \Delta\rho_0 | (1 - \omega) / \omega] - AC_0^{-2} R_c^{-4}. \qquad (1)$$

Here $1 - \omega = V_0 / V_c = \rho_c / \rho_f$, $V_0 = b N_0$ is the proper volume of all fluctuation clusters; $b = 4/3 \pi R_c^{-3}$ is the volume of single density fluctuation cluster; $\rho_f = \rho_c / (1 - \omega)$ is the density of substance inside fluctuation; A is parameter, which characterises the interaction energy between fluctuation clusters at the distances $r > R_c$. On the basis of the expression (1) the coexistence curve (where $R_c^{-1} = t^\nu \Sigma b_n \Delta\mu / t^{\beta\delta}$ [1]) can be written as:

$$(\rho - \rho_c) / \rho_c = dF_1 / d\mu = \pm B_0 t^\beta \quad B_1 t^{2\beta} \quad B_2 t^{\beta\nu} \quad .... \qquad (2)$$

In the equation (2) the second term depends on the density of substance inside the fluctuation clusters. That is, it depends on the interacting forces between the substance molecules inside the fluctuations. The third term depends on the attracting forces between fluctuation clusters at distances $r > R_c$. The form of the equations (1) and (2) has been proved during investigations of coexistence curve for many liquids with different critical temperatures (for instance, He ($T_c = 5.1$ K), CO_2($T_c = 304.3$ K), $C_2 F_3 Cl_3$ ($T_c = 487.11$ K) etc.). Analysis of these data has shown that the density ρ_f of substance inside fluctuation changes from $\rho_f = \rho_c$ (He) to $\rho_f = 2.6 \rho_c$ ($C_2 F_3 Cl_3$) depending on the critical temperature T_c of substance. Moreover the constant A of interaction in (1) also increases.

[1] A.Z. Patashinskii and V.L. Pokrovskii, Fluctuation Theory of Phase Transition (Pergamon, Oxford, 1979).
[2] I.D. Van der Waals, F. Konstamm, Thermostatic Course (ONTI, Moscow, 1936).
[3] A.D. Alekhin, Institute of Higher Education Proceedings. 3, 103 (1983).